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Thermal effect on thermoluminescence response of hydroxyapatite

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HIGHLIGHTS

- HAp powders were obtained by precipitation method.
- Enhancement of TL response of HAp was observed.
- Decomposition phase of HAp at 900 °C was observed.
- Calcination temperature on TL response was analyzed.
- Fading of HAp calcined at 900 °C was performed showing 5% during 134 days.

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ABSTRACT

This paper presents the experimental results of the thermoluminescence (TL) induced by gamma radiation in synthetic hydroxyapatite (HAp) obtained by the precipitation method, using $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ and calcined at different temperatures. The structural and morphological characterization was carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. TL response as a function of gamma radiation dose was in a wide range, where intensity was enhanced in the sample annealed at 900 °C, which tricalcium diphosphate (TCP) phase appear. Fading of the TL was also studied.

1. Introduction

It is known that hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], is the main inorganic component of bones and teeth, and it is synthesized in the laboratory as a biomaterial used in implants and strengthening bones (Bakan et al., 2013, Godfrey-Smith and Pass, 1997, Tas, 2001). Pure hydroxyapatite can be obtained by reactions in aqueous systems or solid state reactions (Hayek and Newesely, 1963, Hench, 1998, LeGeros, 1984, LeGeros, 1991, Martínez-Valencia et al., 2008, Sastre et al., 2004). However, when it is prepared by aqueous precipitation systems or hydrolysis methods, is important the formulation of the appropriate precursors amounts to achieve a fully stoichiometric hydroxyapatite (molar ratio Ca/P = 1.67) because sometimes, a hydroxyapatite with calcium deficient is obtained (Hench and Wilson, 1999). Another advantage of the precipitation method is a simple process, suitable for doping and low production cost, but also can be prepared particles of uniform small size, because the precipitants are formed slowly and uniformly throughout the solution during the precipitation process (Robertson, 1973, Saeri, 2003). The theoretical equation of the precipitation method of hydroxyapatite synthesis was proposed by Hayek and Newesley (1963), and can be represented by the following reaction:

$$10Ca(NO_3)_2 \cdot 4H_2O + 6(NH_4)_2HPO_4 + 8(NH_4)OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 46H_2O \quad (1)$$

Hydroxyapatite formation by this method is sensitive to the concentrations of each precursor and the pH of the reaction. The precipitation temperature varies in a range from room temperature to 100 °C. On the other hand, the decomposition of HAp proceeds in two stages: reversible expulsion of water producing oxyapatite (OA), and irreversible decomposition to HAp yielding calcium phosphates. Whereas the first decomposition stage has no significant effect on the properties of HAp ceramics, the other leads to modify the structural and functional properties. Water and powdered HAp begin to be separated already at 1173 K.

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The water is liberated gradually, and hydroxyoxyapatite $Ca_{10}(PO_4)_6O_x(OH)_{2(1-x)}$ (HOA) with a gradually decreasing content of OH groups is formed (Cihlar et al., 1999). Frequently the decomposition products from the HOA are described as TCP-tricalcium phosphates ($Ca_3(PO_4)_2$), TCP-tetracalcium phosphate ($Ca_4(PO_4)_2$) and H_2O. TCP, with a Ca/P ratio 1.5, has been used for different applications (Román-López et al., 2014, Rivera, 2012). In the last decades, TCP doped with Dy or Eu is suggested as a good material to be used in thermoluminescent applications (Madhukumar et al., 2007).

The thermoluminescence of hydroxyapatite (HAp) is particularly interesting because HAp is a constituent of human bone, in this connection, significant advances have been made in developing of thermoluminescent materials during de last two decades (Rivera, 2011). The most important application of TL lies in high dose of ionizing radiation dosimetry. There has been a great demand for the development of new types of thermoluminescent dosimeter (TLD) for measuring high doses. Alvarez et al. (2014), synthesized hydroxyapatite by the sol–gel method to determine the thermoluminescence characteristics, and they found that hydroxyapatite obtained by this method may could be used in gamma radiation dosimetry applications.

The aim of the present work was to determine the effect of thermal decomposition in the thermoluminescent response of hydroxyapatite calcined at different temperature obtained by precipitation method for its possible application in ionizing radiation dosimetry applications.

2. Materials and methods

The hydroxyapatite (HAp) powders were prepared by precipitation method, using calcium nitrate tetrahydrated ($Ca(NO_3)_2 \cdot 4H_2O$) and ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as precursor salts and ammonium hydroxide (NH_4OH, ammonia water) as precipitant agent and pH control. With the salts were formed separate solutions of 0.5 M and add to calcium nitrate solution (47 gr of $Ca(NO_3)_2 \cdot 4H_2O$ in 400 ml distillated water) the ammonium hydroxide (15.78 gr of $(NH_4)_2HPO_4$ in 240 ml distillated water) until the pH was maintained at 10 ± 0.2. After this, the solution was added dropwise using a peristaltic pump the ammonium hydrogen phosphate solution until obtain the Ca/P ratio of 1.67 with continuously and vigorous magnetic stirring, to ensure homogenous mixing. The temperature and pH were maintained at 60 ± 0.3 °C and 10 ± 0.2, respectively. The system reaction synthesis to obtain the equilibrium of reaction according to Eq. (1), was kept under magnetic stirring for 1/2 h, thereafter, the suspension was filtered and washed with 2.5 l of deionized water, which was preheated to 70 °C. The precipitate was placed in a muffle furnace maintained at 80 °C for 24 h. Finally, the fresh hydroxyapatite powder was submitted at different calcinations temperatures, i.e., at 300 °C, 700 °C and 900 °C for 1 h. Morphological characteristics of the powders were obtained using a scanning electron microscope SEM (Jeol 6400) using a tungsten filament. For these studies, samples were coat with a thin Cu layer prior to this analysis. The crystallographic phases of the samples were characterized by X-ray diffraction (XRD) technique in a Siemens D-5000 X-ray with source radiation of $\lambda = 0.15406$ nm from a Cu target and using Ni-filtered in the 2θ range of 20°–55°. Previous to gamma irradiation processes, HAp powders were submitted to a thermal treatment at 300 °C during 30 min in order to erase any undesirable information. The gamma irradiation processes was carried out with Co-60 gamma ray source facility (25–100 Gy). Using a Co-60 Gamma cell 220 source at a dose rate of 240 Gy/h. The irradiation was made under electronic equilibrium in plexiglas with approximately 3% of uncertainty. In order to obtain statistical data 100 mg of HAp powder and was divided in four aliquots, with 25 ± 0.5 mg for each one. Four aliquots were submitted 9 times under gamma radiation absorbed dose at 25, 50, 75 and 100 Gy, respectively. Thermoluminescent readings were made using a Bicron 3500TL analyzer coupled to a personal computer in order to process and analyze the glow curves data. The heating rate of the TL analyzer was kept at 10 °C/s for all readings. The TL emission was integrated from room temperature (RT) up to 350 °C. In order to reduce the thermal noise, resulting from the heating planchet of the TL reader, readings were made under nitrogen atmosphere. In order to obtain the TL fading characteristics, the sample calcined at 900 °C was irradiated at 50 Gy with gamma irradiation, and storage at room temperature under normal and visible light conditions during 134 days.

3. Results

Morphological and structural characteristics, and thermoluminiscent response are shown and discussed in this section. The morphology of un-calcined and samples calcined at 300, 600 and 900 °C are shown in Fig. 1. The calcination processes of HAp powders was carried out by scanning electron microscopy (SEM). Micrographs of fresh powders showed very fine particles with aggregates (Fig. 1a), maybe in the nanometer range. When the powder is calcined at higher temperatures a slight increase of particle size up to 900 °C is observed, where a slight sintering of aggregates is appreciated (Fig. 1d). Morphology of HAp obtained by precipitation method are very similar than those reported in literature by Alvarez et al. (2014), they obtained similar morphologies in the synthetic hydroxyapatite obtained by sol–gel method when the samples were calcined at 1200 °C.

Fig. 2 shows the X-ray diffraction patterns of HAp un-calcined and calcined samples at 300, 700 and 900 . The diffraction peak positions and relative intensities of all the samples are in good agreement with hexagonal HAp crystalline phase (space group P63/m (176)) according to JCPD card Nr. 75-0565, were there are several major peaks at 31.7°, 32.9° and 25.87°, that correspond to the planes (211), (300) and (003), respectively, and other lower intensity but well defined, corresponding to minor reflections or may be other minor decomposition phases. Roman-Lopez et al. (2014), determined the impurities effect on crystallinity of natural apatites, where they found that the impurities affect the crystallinity index determined by the displacement of the peaks. In this case a displacement of peaks as a function of temperature is not appreciated, only the occurrence of the thermal decomposition phase is observed.

X-ray diffraction patterns of HAp powders calcined at temperatures below 700 °C do not show considerable changes in the phase. As it can be seen in Fig. 2, samples calcined at 900 °C appear in the tricalcium phosphates (TCP) ($Ca_3(PO_4)_2$) phase as product of the decomposition of the hydroxyapatite; this similar effect was observed Liu et al. (2001) when they calcined HAp, this effect was also reported by Kim et al. (2004).

The thermoluminescent analysis corresponding to the un-calcined and calcined samples exposed to gamma radiation absorbed dose are shown in Fig. 3. TL glow curve of HAp obtained at a temperature lower than 900 °C is not present at any TL glow curve. The highest TL intensity was recorded for the 900 °C calcined sample.

As shown in this figure TL intensity value shows variation with calcination temperature. The calcined sample exhibit two thermoluminescent peaks, the first peak centered at around 200 °C and the second one which reaches a maximum peak at 260 °C approximately. These TL peaks indicate two different sets of traps are present. As it can be seen in this figure, TL intensity was